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NEWS

Highlights from recent literature

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Each issue of *Gold Bulletin* contains key highlights from the research and patent literature. Authors who publish high-quality work in other journals are invited to send a copy of their publication to the Editor for inclusion in the next issue.

Electronics

Effects of alloying elements on microstructure and thermal aging properties of Au bonding wire

A team from South Korea has studied the effects of alloying elements Cu and Ni on the microstructure and the thermal aging properties of Au bonding wire (*Microelectronics Reliability*, volume 51, issue 12, December 2011, pp. 2250–2256). The thermal aging properties of samples bonded with an Al pad and annealed at 200°C for durations ranging from 0 to 300 h was investigated using mechanical tests. Both of the alloyed specimens showed higher thermal aging properties than the 4-N Au-bonded specimen. The Cu-alloyed Au bonding wire formed, at the Au–Al interface, a discontinuous Cu-rich layer that was considered to have delayed the growth of the Au–Al intermetallic compound (IMC). Meanwhile, at the Au–Al interface, the Ni-alloyed Au bonding wire formed secondary phase particles that were believed to have improved the bonding strength by interrupting microcrack propagation.

Effect of gold content on the microstructural evolution of SAC305 solder joints under isothermal aging

Au over Ni on Cu is a widely used printed circuit board (PCB) surface finish, under bump metallization, and component lead metallization. It is generally accepted that less than 3 wt% Au in Sn–Pb solder joints inhibits formation of detrimental IMC. However, the critical limit for Au content in Pb-free solder joints is not well established. Three surface-mount package platforms, one with a matte Sn surface finish and the others with Ni/Au finish, were soldered to Ni/Au-finished PCB using Sn-3.0Ag-0.5Cu (SAC305) solder, in a realistic manufacturing setting. The assembled boards were divided into three groups: one without any thermal treatment, one subjected to isothermal aging at 125°C for 30 days, and the third group aged at 125°C for 56 days. Representative solder joints were cross-sectioned and analyzed using scanning electron microscopy and energy-dispersive x-ray spectroscopy to investigate the evolution of the solder joint morphology as a function of Au content and isothermal aging. It was found that, if Cu is available to dissolve in the solder joint, the migration of $AuSn_4$ from the bulk to the interface as a result of thermal aging is mitigated (*Journal of Electronic Materials*, volume 41, number 2, pp. 224–231, doi:10.1007/s11664-011-1744-4).

Organic electronics on natural cotton fibers

In *Organic Electronics* (volume 12, issue 12, December 2011, pp. 2033–2039), an international research team discusses the nanoscale modification of natural cotton fibers with conformal coatings of gold nanoparticles, the deposition of thin layers of the conductive polymer poly(3,4-ethylenedioxithiophene), and a combination of these two processes were employed to increase conductivity of plain cotton yarns. Their approach was designed to fabricate two classes of devices: passive devices such as resistors obtained from electrically conductive cotton yarns, and two types of active devices, namely organic electrochemical transistors and organic field-effect transistors. The detailed electrical and mechanical analysis performed on treated cotton yarns revealed that they can be used as conductors still maintaining a good flexibility. The study has the potential for integration of organic electronics and traditional textile technology and materials.

Microcrystalline-to-amorphous gold alloy and plated film, and plating solution for those, and plated film formation method

This patent from the University of Waseda (US2012031764 A1) relates to a microcrystalline-to-amorphous gold alloy-plated film reportedly having excellent electrical properties and excellent mechanical properties. Physical properties including both the advantageous properties of a crystalline structure and the advantageous properties of an amorphous structure can be obtained by allowing a microcrystalline phase and an amorphous phase to exist in a mixed state at a specific ratio. The average particle diameter of the microcrystals is 30 nm or smaller, the volume fraction of the microcrystals is 10 to 90%, and the knoop hardness is Hk 180 or more. In the film, hardness and abrasion resistance can be improved while maintaining a good specific resistivity value and chemical stability both inherent to gold at practically insignificant levels. Therefore, the film is useful as a material for connecting an electric or electronic component such as a connector and a relay.

Catalysis

The promoting effect of adsorbed carbon monoxide on the oxidation of alcohols on a gold catalyst

Researchers at Leiden University, The Netherlands have exploited the capacity of a gold electrocatalyst to adsorb CO irreversibly and to act as a promoter of the oxidation of alcohols in aqueous alkaline media and of methanol in particular. The CO significantly lowers the onset potential for catalysis in this reaction, leading to enhanced formation of the main methanol oxidation products. The work was published in *Nature Chem*. 2012. (doi:10.1038/nchem.1221)

Electrocatalytic hydrogen redox chemistry on gold nanoparticles

This work by Mathias Brust and Gabriel Gordillo (*J. Am. Chem. Soc.*, 2012, 134 (7), pp. 3318–3321, doi:10.1021/ja2096514) relates to the electrocatalytic behavior of gold nanoparticles. Electrocatalytic proton reduction leading to the formation of adsorbed molecular hydrogen on gold nanoparticles of 1–3 and 14–16 nm diameter stabilized by 1-mercapto-undecane-11-tetra(ethyleneglycol) has been demonstrated by cyclic voltammetry using a hanging mercury drop electrode. The nanoparticles were adsorbed to the electrode from aqueous dispersion and formed robust surface layers transferrable to fresh base electrolyte solutions. Unique electrocatalytic proton redox chemistry that had no comparable counterpart in the electrochemistry of bulk gold electrodes was observed. Depending on size, the nanoparticles had a discrete number of electrocatalytically active sites for the two-electron/two-proton reduction process. The adsorbed hydrogen formed was oxidized with the reverse potential sweep. These findings were claimed to represent a new example of qualitative different behaviors of nanoparticles in comparison with the corresponding bulk material.

Gold catalysis for organic synthesis: opportunities abound

In this journal preface (*Synlett* 2012; 23: 46–48), Dean Toste introduces the use of gold catalysis for organic synthesis. He explains how the reactivity of homogeneous gold catalysts has been explored, developed, and harnessed by organic chemists. Among other reactivities, gold complexes can act as mild π-acid catalysts, participate in backbonding to generate intermediates with unique reactivity, and promote oxidative coupling reactions. Modification and tuning of the ligands in these complexes can modify reactivity and result in highly selective reactions. It is considered that this relatively young field is still developing and entirely new modes of reactivity are being discovered.

Metallurgy

Gold alloy with improved hardness

A new patent from Swatch Group (WO2012000803 A2) relates to a gold alloy with improved hardness. It comprises at least 75 % gold, from 0.5 to 2.1% aluminum capable of forming precipitates with the gold, an additional metal capable of favoring a stable face-centered cubic structure, and capable of increasing the solubility of the aluminum in the gold, and one such precipitate selected in order to obtain a hardness of greater than 250 HV. The selected precipitate of aluminum with the gold is the precipitate of aluminum and of gold Al_2Au_5; it comprises 0.5 to 2.1% aluminum and a supplement of additional metal comprising a majority of silver. The process for obtaining this alloy regulates a controlled growth of this precipitate during a structural tempering consecutive to a dilution and to a quenching. The invention relates to the use of the precipitate of aluminum and of gold Al_2Au_5 for the hardening of a gold alloy, as well as a watch or jewelry component made in this alloy.

Nanotechnology

Synthesis of bimetallic gold–silver alloy nanoclusters by simple mortar grinding

This recent paper reports on the macroscale production of bimetallic Au–Ag alloy nanoclusters through sequential

reduction by simple mortar grinding (*Nanoscale* 2012 Feb 2; 4(4):1280–2). A chitosan biopolymer was used as both a stabilizing and reducing agent. The nanoclusters exhibited excellent catalytic activity toward the reduction of 4-nitrophenol.

Efficiency enhancement of screen-printed multicrystalline silicon solar cells by integrating gold nanoparticles via a dip coating process

Published in *Optical Materials Express* (February 2012, vol. 2, no. 2), this work investigates the use of gold nanoparticles in photovoltaics. Multicrystalline silicon solar cells play an increasingly important role in the world photovoltaic market. Boosting the comparatively low energy conversion efficiency of multicrystalline silicon solar cells would be a significant advancement. In this paper, Au nanoparticles of an optimized size, synthesized by the iterative seeding method, were integrated onto industrially available surface-textured multicrystalline silicon solar cells via a dip coating method. Enhanced performance of the light absorption, the external quantum efficiency, and the energy conversion efficiency were consistently demonstrated, resulting from the light scattering by the size-tailored Au nanoparticles placed on the front surface of the solar cells, particularly in the spectral range from 800 to 1,200 nm, an enhancement of the external quantum efficiency by more than 11% near λ=1,150 nm and the short-circuit current by 0.93% were both observed. As a result, an increase in the energy conversion efficiency up to 1.97% under the standard testing conditions (25°C, global air mass 1.5 spectrum, 1,000 $W m^{-2}$) was achieved. This study opens new perspectives for plasmonic nanoparticle applications for photon management in multicrystalline silicon solar cells.

One-step fabrication of supramolecular microcapsules from microfluidic droplets

Although many techniques exist for preparing microcapsules, it is still challenging to fabricate them in an efficient and scalable process without compromising functionality and encapsulation efficiency. We demonstrated a simple one-step approach that exploits a versatile host–guest system and uses microfluidic droplets to generate porous microcapsules with easily customizable functionality. The capsules comprise a polymer–gold nanoparticle composite held together by ternary complexes. The dynamic yet highly stable micrometer-sized structures can be loaded in one step during capsule formation and are amenable to on-demand encapsulant release. The internal chemical environment can be probed with surface-enhanced Raman spectroscopy. Zhang et al., *Science* 10 February 2012: vol. 335 no. 6069, pp. 690–694

Hybrid graphene–metal nanoparticle systems: electronic properties and gas interaction

In this *Journal of Material Chemistry* paper (*J. Mater. Chem.*, 2011, 21, pp. 15593–15599), the electrical properties of reduced graphene oxide (rGO) decorated with gold and silver nanoparticles were studied. Metal nanoparticles were used to p-dope rGO through charge transfer which causes a potential drop at the metal nanoparticle–graphene interface. Probing by reactive gasses demonstrated that the nanoparticles provide interaction sites, inducing the sensitivity to H_2S and improving the sensitivity to NO_2.

Medical

Gold(III) complexes with oligopeptides functionalized with sulfur donors and used thereof as antitumor agents

This recent patent application (EP2408445) submitted by the University of Padova concerns Au(III) complexes which are able to both maintain the antitumor properties and the lack of nephrotoxic side effects of the previously reported Au(III)-dithiocarbamato complexes, together with an improved bioavailability through the peptide-mediated cellular internalization. The Au(III) complexes described are claimed to show a significant biological activity on human tumor cell lines and, thus, they can be advantageously used as antineoplastic agents. The preparation method and use for the treatment of tumor pathologies of the Au(III) complexes of the invention are described.

Hollow gold nanospheres (HAuNSs) and HAuNSs-loaded microspheres useful in drug delivery

This new US patent application (US2011318415 A1) relates to a near-infrared mediated drug delivery system comprising of microspheres made of polymeric material, each sphere containing hollow gold nanospheres together with drug product. Upon NIR irradiation, the drug product is released from the microsphere.

Gold nanoparticles: preparation, properties, and applications in bionanotechnology

In this review article in *Nanoscale* (doi:10.1039/C1NR11188D), the authors describe how gold nanoparticles (AuNPs) are important components for biomedical applications. AuNPs have been widely employed for diagnostics, and an

increasing use in the area of therapeutics has been seen. In this mini-review, they present fabrication strategies for AuNPs and highlight a selection of recent applications of these materials in bionanotechnology.

Targeting gold nanoshells on silica nanorattles: a drug cocktail to fight breast tumors via a single irradiation with near-infrared laser light

This paper in *Advanced Materials* (24: 755–761. doi:10.1002/adma.201103343) reported how drug-loaded transferrin and poly(ethylene glycol)-functionalized gold nanoshells on silica nanorattles can combine the active targeting, passive targeting, and remote-controlled photothermal therapy together with chemotherapy to completely kill tumor cells via a single irradiation with near-infrared laser light.